III.A.19 Resilient and Thermochemically Stable Sealing Materials for Solid Oxide Fuel Cells

Richard K. Brow
University of Missouri-Rolla
Materials Science & Engineering Department
222 McNutt Hall
Rolla, MO 65409-0330
Phone: (573) 341-6812; Fax: (573) 341-6934; E-mail: brow@umr.edu

DOE Project Manager: Travis Shultz
Phone: (304) 285-1370; E-mail: Travis.Shultz@netl.doe.gov

Objectives

- Develop, characterize, fabricate, and test a hermetic solid oxide fuel cell (SOFC) seal based on a thermochemically stable glass-ceramic system.
- Fabricate seals between SOFC component materials at temperatures below 900°C and characterize stability in oxidizing and reducing environments at temperatures up to 800°C.

Approach

- Optimize glass compositions with the requisite thermal and chemical properties for SOFC seals.
- Develop techniques to produce composite seals using glasses and filler materials (ceramic and metallic) chosen to improve seal resiliency during thermal cycling.
- Characterize the hermeticity of seals after thermal cycling between use temperatures (up to 800°C) and room temperatures.

Accomplishments

- *Promising sealing glasses developed.*
  Several 'baseline' glass compositions have been developed that appear to possess requisite thermal and chemical properties as 'host materials' for resilient composite seals. The glasses have thermal expansion coefficients in the range $10\text{-}12\times10^{-6}/°C$, have low volatility rates in wet forming gas at 750°C, and form well-adhered bonds to stainless steel interconnect materials and to Y-stabilized zirconia (YSZ).
- *Glass-crystallization kinetics studied.*
  We have developed a new thermal analytical technique that provides a quantitative measure of the degree of crystallization of a glass-ceramic material and have used this technique to characterize new SOFC materials.

Future Directions

- *Develop resilient 'composite' sealing materials.*
  We will prepare and characterize composites between baseline glasses and ceramic and metallic fillers to modify the thermal expansion/contraction characteristics of the sealing materials to better survive thermal cycling.
- *Prepare and characterize hermetic seals.*
  We will prepare hermetic seals between YSZ and Cr-steel interconnect alloys using optimized sealing materials and characterize hermeticity using a helium manifold currently under development. Hermeticity will be tested after subjecting the seals to a series of thermal cycles between 750°C and room temperature.

- *Test SOFC cells.*
  The sealing materials will be used to fabricate prototype, operational SOFC cells, and the cells will be thermally cycled between 750°C and room temperature at least ten times to characterize the effects of the seals on cell performance.

Introduction

Planar SOFC configurations are relatively simple to manufacture and have higher power densities and efficiencies than other configurations, but require hermetic seals to prevent mixing of the fuel and oxidant streams within the cell stack and to seal the stack to the system manifold. Within the SOFC stack, an effective seal must have a thermal expansion match to the fuel cell components, must be electrically insulating and must be thermochemically stable under the operational conditions of the stack. The seal should exhibit no deleterious interfacial reactions with other cell components, should be stable under both the high-temperature oxidizing and reducing operational conditions, should be created at a low enough temperature to avoid damaging cell components (under 850°C for some materials), and should not migrate or flow from the designated sealing region during sealing or cell operation. In addition, the sealing system should be able to withstand thermal cycling between the operational temperature and room temperature. That is, thermal stresses that develop because of mismatches in the thermal contraction characteristics of the different SOFC materials must either be reduced to well below the failure strengths of the materials or must be relieved in some fashion.

Approach

The objective of this project, which started in October 2004, is to develop novel glass compositions for resilient glass-ceramic hermetic seals for solid oxide fuel cells. The glasses are based on novel alkaline earth silicate compositions that possess invert molecular structures and so possess the viscosity characteristics to seal at relatively low temperatures, but crystallize to form a thermally stable sealing material. (Invert glasses do not possess the continuous cross-linked silicate structures of more typical silicate glasses.) The 'resiliency' will be obtained by engineering the characteristics of the ceramic and residual glassy phases of the glass-ceramic seal. A ceramic phase will be selected to induce microcracks in the seal upon cooling. The residual glassy phase will be designed to flow and heal those microcracks when the seal is reheated. The controlled release of stress through microcracking and subsequent viscous 'resealing' will allow the seals to survive the stringent thermal cycling requirements for SOFCs.

Crystallized glasses with desirable thermal and chemical properties will be prepared and evaluated at the University of Missouri-Rolla. The glasses will be sealed (as thin films) to SOFC component materials, including YSZ electrolytes and ferritic stainless steel interconnect materials. Long-term stability experiments will be performed, as will thermal cycling experiments. The electrical characteristics of the thin-film seals will be evaluated, and *in situ* impedance measurements under simulated SOFC use conditions will be made to provide information about the long-term thermochemical stability of seal couples.

Results

We have developed and characterized several glass compositions that appear to possess the chemical and thermal properties desirable for a host matrix for resilient composite sealing materials. The glasses are based on the alkaline earth-zinc-silicate system, with other oxides added to control crystallization behavior and to tailor thermal properties. Certain compositions possess good thermal expansion matches to YSZ, before and after crystallization. For example, Figure 1 shows the expansion difference between a crystallized glass (designated 'glass #27') and YSZ, after heat-treatment at 750°C for up to 28 days. The expansion characteristics of the glass-ceramic do not change significantly below about 600°C. Above 600°C, the expansion coefficient of the glass-ceramic increases relative to the YSZ. We believe this is related to the expansion characteristics of the residual glass. X-ray diffraction analyses of the crystallized glasses indicate that pyrosilicate and orthosilicate (e.g., $Ca_2ZnSi_2O_7$, $CaSrAl_2Si_2O_7$, Sr_2SiO_4, etc.)

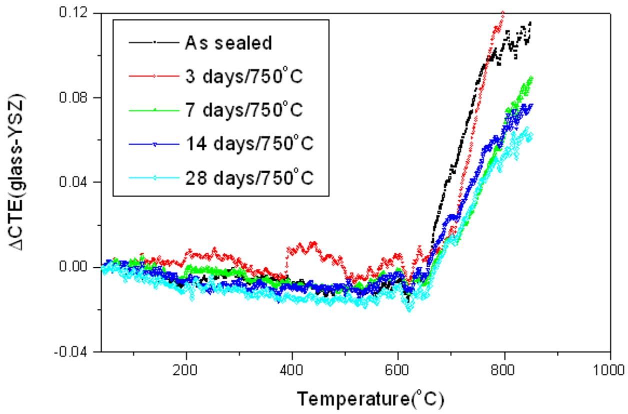

Figure 1. Thermal Expansion Characteristics of Sealing Glass #27 after Being Held at 750°C for up to 28 Days

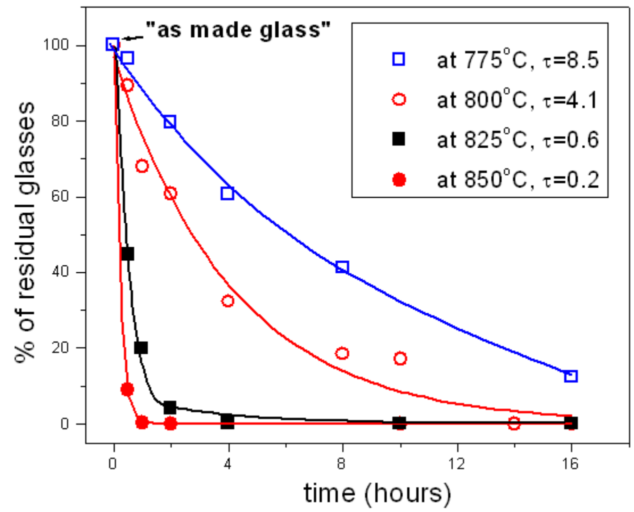

Figure 2. The Amount of Residual Glass in Glass #27 after Thermal Treatments in Air for Different Times and Temperatures, as Determined by Differential Thermal Analysis

phases dominate. Weight loss measurements from glasses held in wet forming gas at 750°C for up to 28 days indicate that the glass-ceramics are thermochemically stable.

We have studied the crystallization kinetics of the sealing glasses using a new quantitative differential thermal analytical (DTA) technique developed at the University of Missouri-Rolla [1]. Glasses are held at different temperatures for various times and a DTA scan is collected. The area under the crystallization peak is then used as a relative measure of the amount of residual glass in the heat-treated sample. A larger crystallization peak means more residual glass after heat treatment, whereas no DTA crystallization peak means no residual glass in the sample. Figure 2 shows a summary of the DTA analyses of glass #27. Similar studies are presently underway to evaluate other compositions and to characterize how the addition of 'filler materials' affects the crystallization kinetics of the base glasses.

The glasses adhere well to YSZ and to Cr-steel interconnect alloys. Figure 3 shows a scanning electron micrograph image of the interface of a glass #27/E-brite seal after four days at 750°C. (Image provided by Ron Loehman, Sandia National Labs.) No evidence for the formation of deleterious interfacial reaction products is evident, in contrast to reports on BaO-containing glasses [2]. Adhesion tests indicate bond strengths of 40 MPa, with failure in the glass, not at the interface.

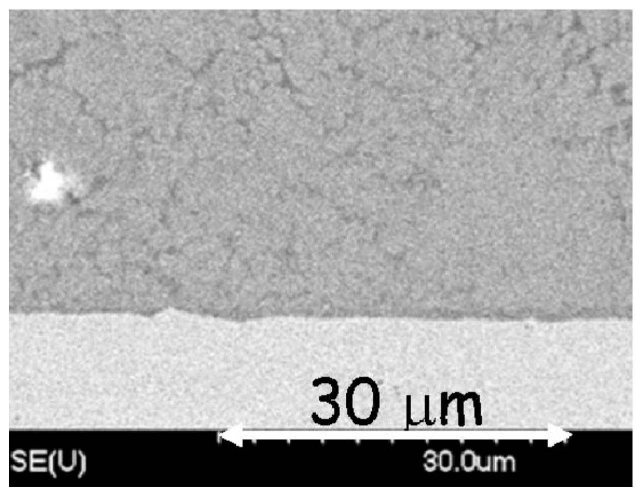

Figure 3. Scanning Electron Micrograph of a Glass #27 (top)-E-brite (bottom) Interface, after Four Days at 750°C (From Ron Loehman, Sandia National Labs)

Conclusions

- We have developed glasses that, when crystallized, possess thermal properties that make them candidates for SOFC seals.
- We have bonded these glasses to YSZ and to Cr-steel interconnect alloys, including E-brite, Crofer APU 22 and 430SS.
- Protocols for preparing glass/filler composite sealing materials are presently being developed.

FY 2005 Publications/Presentations

1. S. T. Reis, R. K. Brow, "Designing Sealing Glasses for Solid Oxide Fuel Cells," Proceedings of the ASM Materials Solution Conference, Fuel Cells: Materials, Processing and Manufacturing Technologies, Columbus, OH, October 18-20, 2004.
2. R. K. Brow and S. T. Reis, "Designing Sealing Glasses for Solid Oxide Fuel Cells," ASM Materials Solution Conference, Fuel Cells: Materials, Processing and Manufacturing Technologies, Columbus, OH, October 18-20, 2004 (INVITED).
3. S. T. Reis*, R. K. Brow, and P. Jasinski, "Developing Glass Seals for Solid Oxide Fuel Cells," 2nd International Symposium on Solid Oxide Fuel Cells: Materials and Technology, 29th International Cocoa Beach Conference and Exposition on Advanced Ceramics and Composites, Cocoa Beach, FL, January 23-28, 2005.
4. R. K. Brow*, T. Zhang, and S. T. Reis, "Thermochemically Stable Sealing Materials for Solid Oxide Fuel Cells," SECA Core Technology Workshop, Tampa, FL, January 27, 2005.
5. R. K. Brow*, "Glass Seals for Solid Oxide Fuel Cells," Iowa State Materials Science & Engineering Seminar, Ames, IA, March 3, 2005 (INVITED).
6. T. Zhang*, S. T. Reis, and R. K. Brow, "Glass Seals for Solid Oxide Fuel Cells," 107th Annual Meeting of the American Ceramic Society, Baltimore, MD, April 10-13, 2005.
7. R. K. Brow, "Thermochemically Stable Sealing Materials for Solid Oxide Fuel Cells," Solid State Energy Conversion Alliance 6th Annual Workshop, Pacific Grove, CA, April 18-21, 2005 (INVITED).
8. R. K. Brow, "Sealing Glasses for Solid Oxide Fuel Cells," 17th University Conference on Glass Science and 1st International Materials Institute Workshop on "New Functionality in Glasses", Penn Stater Conference Center Hotel, State College, PA, June 26-30, 2005 (INVITED).

References

1. C. S. Ray, S. T. Reis, R. K. Brow, W. Höland, W. Rheinberger, "A New DTA Method for Measuring Critical Cooling Rate for Glass Formation," *Journal of Non-Crystalline Solids*, **351** 1350-58 (2005).
2. N. Lahl, D. Bahadur, *et al*. (2002) *J. Electrochem. Soc*. 149[5] A607-A614.